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Investigation of the degradation of cresols in the treatments with ozone

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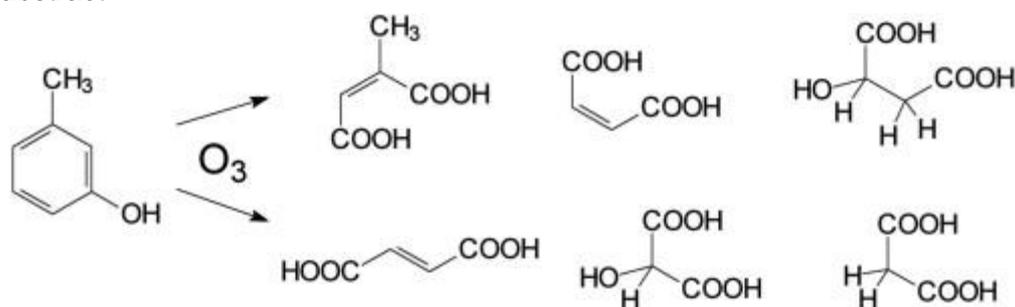
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Abstract

The reaction between ozone and the three cresol isomers was investigated in pure water. Cresols were selected as model substrates representing an important component of humic material. Cresols carry both a hydroxyl and a methyl group, each theoretically increasing the reactivity of ozone with the aromatic ring. Direct comparison of the aromatic ring and the methyl group reactivities was made possible by the analysis of reaction products. The substrate degradation kinetics was studied by preparing aqueous solutions of each cresol and treating them with ozone for increasing time periods. It had been hypothesized that hydroxybenzaldehydes and hydroxybenzoic acids could be possible degradation intermediates of cresols. To verify this hypothesis, the degradation kinetics of three hydroxybenzaldehydes and two hydroxybenzoic acids were also studied. The reaction products were studied using gas chromatography (GC)-electron capture negative ionization (ECNI)-mass spectrometry (MS) analysis after direct derivatization of the samples with 5-chloro-2,2,3,3,4,4,5,5-octafluoro-1-pentyl chloroformate (ClOFPCF). This new analytical approach enables the extraction and analysis of highly polar polycarboxylic and hydroxycarboxylic acids, as well as highly polar aldehydes and hydroxy aldehydes that are difficult to extract and measure using conventional methods. As such, this new approach offered insights into ozone reaction intermediates that had been previously hypothesized, but not confirmed. Several highly hydrophilic degradation intermediates were identified, including malic, citraconic, itaconic, malonic, methylmuconic, and tartronic acid, but no hydroxybenzaldehydes were observed. The results support a 3-stage mechanism previously hypothesized, which involves ring-opening of the phenolic group, followed by the generation of several intermediates of increasing oxidation state, finally leading to relatively stable products, such as malonic and oxalic acids. We demonstrated that oxidation of the methyl group does not occur during cresol degradation.

Graphical abstract



Highlights

► Reaction of O₃ with three cresol isomers used as model compounds for humic material. ► Ozone reacts preferentially with the aromatic ring, not the methyl group. ► Highly hydrophilic reaction by-products are formed from cresols after ring-opening. ► Chloroformate derivatives of degradation intermediates are identified by GC-ECNI-MS.

Keywords

- Cresol;
- Ozone;
- Degradation intermediate;
- Disinfection by-products;
- DBPs;
- Chloroformates

1. Introduction

Disinfection of drinking water is important to eliminate the human health threat caused by the pathogenic microorganisms that can be present in natural waters. However, disinfectants can react with natural organic matter (NOM) and other constituents to form disinfection by-products (DBPs), several of which are genotoxic, cytotoxic, or carcinogenic (Richardson et al., 2007). Ozone is a popular disinfectant because it is effective for killing microorganisms and it significantly reduces the formation of halogenated DBPs, with the exception of water sources containing high bromine levels (Haag and Hoigne, 1983; Glaze and Weinberg, 1993; Richardson et al., 1999a; von Gunten, 2003a). The most common ozonation by-products are aldehydes, ketones, and short-chain carboxylic acids (Glaze and Weinberg, 1993; Richardson et al., 1999b; Richardson, 2011). These DBPs constitute a large fraction of the assimilable organic carbon (AOC) that can contribute to bacterial regrowth (Glaze, 1986; Ramseier et al., 2011); because of this, many ozone drinking water plants use biological filtration to remove AOC before the finished water enters the distribution system.

In general, ozone reacts with NOM by two primary mechanisms, generally classified as (i) $\cdot\text{OH}$ radical reactions and (ii) molecular O_3 reactions (von Gunten, 2003b), whose prevalence is due to multiple factors. The $\cdot\text{OH}$ radical is a stronger oxidant than molecular ozone, and it is less selective in its reactions, such that it will react with many different functional groups. The formation of $\cdot\text{OH}$ radicals depends on (i) the presence of hydroxylic and peroxidic ions, (ii) the ozone concentration, and (iii) the conversion kinetics of ozone into $\cdot\text{OH}$ radicals (Hoigne, 1997). Molecular ozone may react by three different mechanisms: (i) cycloaddition to double bonds, (ii) electrophilic attack, and (iii) nucleophilic attack (Glaze and Weinberg, 1993).

Investigations on ozone reactivity have used toluene and xylene as model substrates to simulate parts of NOM (Razumovskii, 2006; Hoigne and Bader, 1983a). It had been hypothesized that ozone may react with the methyl groups to progressively produce phenols, aldehydes, and lastly benzoic acids; thereafter the aromatic ring may be attacked. However, recent results demonstrate that reactions of ozone with methyl groups and double bonds can occur simultaneously and competitively (Razumovskii, 2006). The presence of an electron-donating group, such as a methyl group, increases the chance of a nucleophilic attack on the aromatic ring. Moreover, the presence of more than one methyl substituent in xylenes inhibits their oxidation, while promoting the reaction between ozone and the aromatic ring (Razumovskii, 2006).

Phenols have also been extensively studied as model substrates, and many oxidation products have been identified, including several carboxylic acids (e.g., formic, acetic, oxalic, maleic, fumaric, tartronic, glycolic, muconic, glyoxylic acid), aldehydes (e.g., glyoxal, muconaldehyde, formaldehyde), and others (e.g., catechol, hydroquinone, benzoquinone) (Yamamoto et al., 1979; Singer and Gurol, 1983; Hoigne and Bader, 1983b; Huang and Shu, 1995; Mvula and von

Sonntag, 2003; Hsu et al., 2005; Poznyak and Vivero, 2005; Oh et al., 2006; Komissarov et al., 2006; Ramseier and von Gunten, 2009; Jung, 2001).

For cresols, the presence of the hydroxyl group should hinder the reaction of ozone with the methyl substituent and, conversely, promote its cycloaddition to aromatic double bonds, resulting in the formation of ozonide intermediates. In the few studies concerning cresols, the oxidation of the methyl group was not reported, whereas various hydroxylation products of the aromatic ring (methylcatechols, methylhydroquinone, methylbenzoquinone) were identified (Olariu et al., 2002; Coeur-Tourneur et al., 2006). The same products were observed when the electro-Fenton process was used instead of ozone to oxidize cresols (Pimentel, 2010; Pimentel et al., 2008; Oturan et al., 2008). Oxidation of the methyl group in o-, m-, and p-cresols to yield the corresponding benzaldehydes was observed by using TiO₂ photocatalytic treatments (Wang et al., 1998).

Models of humic acid structures assume that several alkylphenolic units are linked in different ways to a macromolecular skeleton (Schulten and Schnitzer, 1993; Kim and Yu, 2007). It is also known that alkylphenolic rings are preferential substrates for ozone attack, due to their conjugated double bond system and the presence of alkyl- and hydroxyl substituents with electron-donating properties (Glaze and Weinberg, 1993). In the present study, we investigated the reaction between ozone and the three cresol isomers, selected as model substrates that represent an important component of humic material. Cresols carry both a hydroxyl and methyl group, each theoretically improving the reactivity of ozone toward the aromatic ring. Extensive analytical work based on an original approach (Vincenti et al., 2010) allowed us to identify several new reaction intermediates and products (citraconic, itaconic, methylmuconic acids), making possible a direct comparison of the aromatic ring and the methyl group reactivities. This analytical approach uses a highly fluorinated alkyl chloroformate to achieve direct derivatization of hydrophilic intermediates in water, followed by extraction of the derivatives, and their subsequent determination at ultra-trace level by electron capture negative ionization (ECNI)-mass spectrometry.

2. Materials and methods

2.1. Chemicals and standard solutions

Pyridine, o-, m- and p-cresol, 2-, 3- and 4-hydroxybenzaldehyde, 2- and 4-hydroxybenzoic acid, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dihydroxybenzoic acid, malic, maleic, malonic, methylmalonic, citraconic, itaconic, fumaric and methylmuconic acids, and 2,2,3,3,4,4,5,5-octafluoropentan-1-ol were purchased from Sigma-Aldrich (Milan, Italy). 5-H-Octafluoropentanoic acid and perfluoroheptane were from Apollo Scientific Ltd. (Bredbury, U.K.). Tartronic acid and 3-hydroxybenzoic acid were purchased from Merck; 3,4-dihydroxybenzaldehyde and indigo trisulphate were purchased from Fluka (Buchs SG, Switzerland).

Separate stock solutions at 3.0 µg/mL were prepared by dissolving the standards in ultrapure water. All standard solutions were stored at 4 °C until use.

2.2. Synthesis of 5-chloro-2,2,3,3,4,4,5,5-octafluoromethylchloroformate

Briefly, 5-chloro-2,2,3,3,4,4,5,5-octafluoro-1-pentyl chloroformate (ClOFPCF) was synthesized from 5-chloro-2,2,3,3,4,4,5,5-octafluoropentan-1-ol, which in turn was synthesized from 5-H-octafluoropentanoic acid. Photo-chlorination of the 5-H-octafluoropentanoic acid, followed by esterification and reduction of the corresponding ethyl ester was then performed.

Further details on the preparation of highly fluorinated chloroformates, together with their stability and safety measures, are provided elsewhere (Vincenti et al., 2004, Vincenti et al., 2005 and Vincenti et al., 2010). The chloroformate solution was added to the aqueous samples under study, achieving direct derivatization of the analytes in water (see 2.4).

2.3. Instrumentation and analysis

A laboratory ozonator was fed by of an O₂ or air tank coupled with a pressure reducing valve. The ozone generator used a UVP Pen-Ray® mercury discharge lamp (Upland, CA), which produced a stable source of 185 nm radiation for the formation of ozone gas. The ozone gas was then diffused into a calibrated vial containing the aqueous solution of cresols or other substrate (semi-batch method). The best ozone yield was obtained using O₂ instead of air and setting the oxygen flow in the range of 20–50 mL/min. These conditions produced 3–4 × 10⁻⁵ mol (1.44–1.92 mg) of ozone per hour of treatment.

A Branson Sonifier II W-450 (Danbury, CT) sonicator, with variable emission power, was used to keep the derivatization reactions under ultrasonic mixing. Details on the devices utilized for the derivatization are provided elsewhere (Vincenti et al., 2005).

A benchtop PerkinElmer TurboMass (Norwalk, CT) spectrometer equipped with an AutoSystem XL gas chromatograph was utilized for most analyses. The quadrupole mass-analyzer had an upper mass limit of 1200 Da. A chemical ionization source was used to acquire ECNI mass spectra. Isobutane was employed as the moderating gas, at a pressure of 50 Pa. The ion source was maintained at the lowest temperature (140 °C), compatible with prevention of analyte condensation.

A DB-5MS (5% diphenyl dimethyl siloxane) capillary column (30-m long, 0.25 mm i.d., 0.25 µm film thickness, Agilent, Folsom, CA) was utilized. The samples were injected by an AutoSystem XL autosampler in the splitless mode at an injection port temperature of 300 °C. The carrier gas (helium) was maintained constant at 1 mL/min. The oven temperature was programmed as follows: isothermal at 35 °C for 2 min, from 35 °C to 300 °C at 15 °C/min, isothermal at 300 °C for 5 min. The transfer line was maintained at 200 °C.

An Agilent 5973 quadrupole mass spectrometer equipped with an Agilent 6890 gas chromatograph was employed for some of the competitive kinetics studies. This instrument was equipped with an electron impact (EI) source. The electron energy was set at 70 eV and the filament current at 1 mA. The source temperature was set at 200 °C. A DB-5MS capillary column (30-m long, 0.25 mm i.d., 0.25 µm film thickness) was also used for these measurements. The GC oven temperature program and other conditions were the same as on the PerkinElmer instrument described above.

2.4. Sample preparation

In the ozonation experiments, a 25 mL fresh unbuffered solution of substrate (3.0 µg/mL) was subjected to reaction with ozone for variable periods of time. At the end of the selected ozonation period, a 2 mL aliquot was sampled for the analysis of both reagents and products, while the rest of the solution was discarded, i.e. each solution was sampled only once. A fresh solution was used for each experimental point of the reaction profile, in order not to vary the solution volume and the cresol total content during the ozone treatment.

Once the sampling was completed, the remaining portion of the treated solution was tested by adding a small amount (100 µg) of indigo trisulphate (an efficient ozone quencher with intense blue color, which reacts with ozone to yield immediate decolorization), demonstrating that ozone was instantly and completely consumed in the reaction with the cresol substrate (Bader and Hoigné, 1981).

The 2 mL aqueous aliquot was basified with 200 µL of 1 M NaOH. Then, 150 µL of chloroformate solution was directly added (2 µmol of chloroformate in acetone) while keeping the reaction tube under ultrasonic mixing at optimized power and distance from the emitting tip. Immediately, 5 µL of a saturated (400 mg/L) dicyclohexylcarbodiimide (DCC) solution in pyridine was added. The reaction was allowed to proceed for 3 min under sonication. The reaction products were extracted in *n*-hexane (600 µL) by liquid–liquid extraction. The organic layer was separated, concentrated by a gentle stream of nitrogen and immediately analyzed by GC–MS. All the derivatization products proved stable for at least several hours.

To determine the remaining cresol concentration, the chromatographic peak area arising from the selected *m/z* 320 fragment ion was monitored. The latter fragment generates the most abundant ion in the ECNI mass spectra for all cresol derivatives. This product ion arises from consecutive losses of hydrochloric acid and carbon dioxide from the molecular ion.

In competitive degradation studies, a 5 mL solution containing two cresol isomers at 3.0 µg/mL each was collected in a separatory funnel after ozone treatment for variable intervals. Then, 1 mL of hydrochloric acid (1 M) and 5 mL of dichloromethane were added for extraction. After 1 min of vigorous shaking, the organic phase was separated. To eliminate all water traces in the organic

phase, a small amount of anhydrous Na_2SO_4 was added. One μL of the organic extract was directly injected into the GC–MS instrument.

3. Results and discussion

3.1. Degradation kinetics for cresols

Fig. 1 shows the degradation curves for each of the three cresols, obtained by increasing the exposure time to ozone. The degradation curves do not show an exponential trend, but rather an initial linear decrease followed by an exponential decay. To understand the degradation kinetics, several experimental aspects should be taken into account. (a) The sample volume was 25 mL and the initial substrate concentration was $3.0 \mu\text{g/mL}$, resulting in a total cresol content of about 7×10^{-7} mol. (b) The constant oxygen flow was about 20–30 mL/min, producing 6×10^{-7} mol/min (0.029 mg/min) of ozone. (c) The ozone gas was slowly bubbled (diffused) over time into the cresol solution, making the contact time between ozone and the cresol solution short. Therefore, ozone concentrations are low with respect to the substrate. (d) The reaction kinetics are fast, virtually consuming all dissolved ozone, as demonstrated by indigo trisulphate addition, not showing decolorization. Thus, the initial linear decrease of the cresol concentration exhibited in Fig. 1 is likely to be the consequence of the substrate in excess with respect to ozone. To confirm this hypothesis, additional tests were conducted with increased cresol concentrations in the reacting solution ($5 \mu\text{g/mL}$ and $15 \mu\text{g/mL}$, respectively). Different ozonation periods were also tested. At identical ozonation intervals, the absolute amount of consumed cresol was approximately constant, while the percentage of unreacted substrate increased proportionally to the increased substrate concentration. This confirms that most of the dissolved ozone reacted promptly, independent of the chosen substrate, and explains why the degradation rates for the three cresol isomers appear similar, at least until their concentration is high.

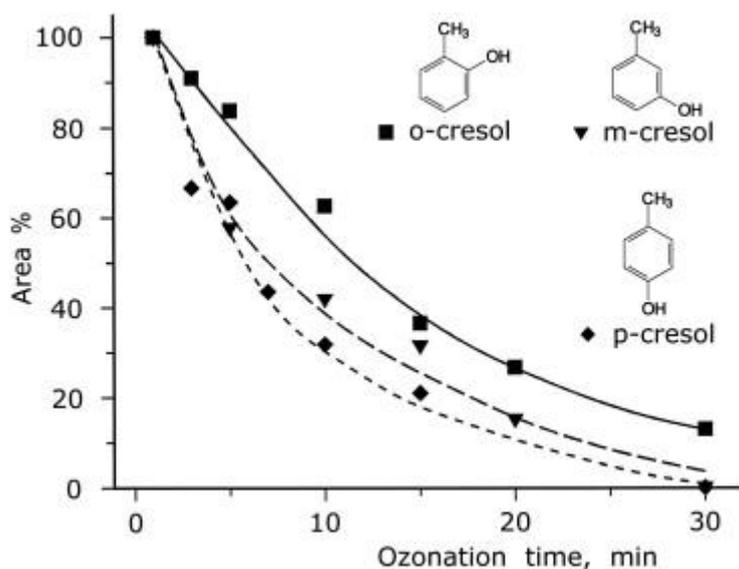


Fig. 1. Kinetic degradation of three separate cresols (7×10^{-7} mol) treated with 6×10^{-7} mol/min of ozone.

A weak selectivity among the cresol isomers was observed as follows: para- > meta- > ortho-. These results are partially surprising because the meta- isomer is supposed to be the most reactive, since three un-substituted positions of the ring (2, 4 and 6) are activated by methyl and hydroxyl electron-donating groups. In addition, two ortho-positions to the hydroxyl group are available for $\cdot\text{OH}$ radical attack (Galstyan et al., 1992). The para-cresol isomer has four positions similarly activated by one electron-donating group, either the methyl or the hydroxyl. The ortho-isomer should be the least reactive because it has only one free position ortho to the hydroxyl group, as was experimentally observed. In order to verify the relative reaction rates of meta- and para- isomers, competitive degradation kinetics studies were performed.

Two analytical methods were used to determine the residual cresol concentrations in competitive degradation experiments carried out with mixtures of m- and p-cresol and mixtures of o- and p-cresol: (i) 2 mL of the ozonated samples were derivatized with ClOFPFCF and subsequently analyzed by GC-ECNI-MS; (ii) underivatized cresols were extracted with dichloromethane from the reacting solution, after HCl addition, and directly injected into the GC-MS. In fact, cresols in their acidic form are sufficiently hydrophobic to be easily extracted from water. However, the meta- and the para- isomers could not be efficiently distinguished using the latter method, because of their GC peak co-elution and tailing, together with virtually identical electron impact mass spectra. Therefore, the competitive degradation of m- and p-cresols was determined only by analyzing their derivatization products, whose GC peaks are clearly separated.

Fresh solutions were used to determine each point of the competitive degradation curves. The normalized areas were calculated with respect to the values obtained from non-ozonated samples. The curves reported in Fig. 2 indicate that p-cresol degradation occurs faster than that of m-cresol,

which mirrored the order of reactivity seen with the individual cresols (Fig. 1). This result is corroborated from the measurement of the m-cresol vs. p-cresol abundance ratio, which shows a linear increase with increasing reaction time.

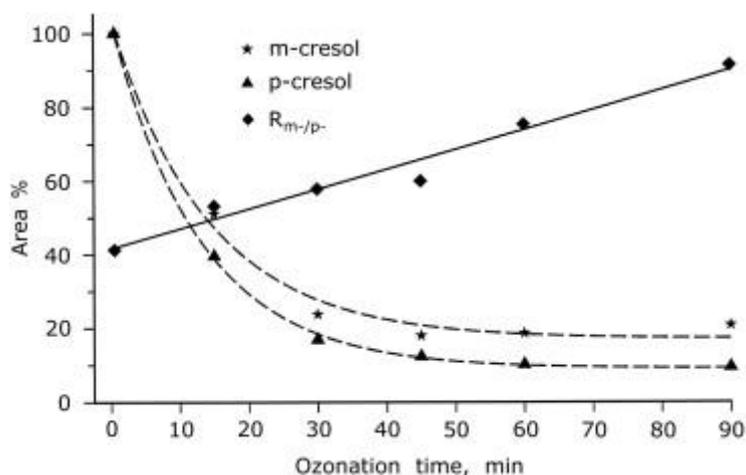


Fig. 2. Competitive degradation of m-cresol and p-cresol (7×10^{-7} mol treated with 6×10^{-7} mol/min of ozone). GC peak areas are compared with initial ones (100%) and the ratio of their absolute value was calculated ($R_{m-/p-}$).

In accordance with the reactivity order previously reported, the curves observed for o-cresol vs. m-cresol or vs. p-cresol confirm that o-cresol degradation takes place at a lower rate than either m- or p-cresol.

3.2. Investigation of hydroxybenzaldehydes and hydroxybenzoic acids as possible intermediates

Hydroxybenzaldehydes and hydroxybenzoic acids are possible degradation intermediates of cresols, arising from oxidation of their methyl group (Wang et al., 1998). In order to verify the ozone reactivity of these substances with respect to cresols, the degradation kinetics of three hydroxybenzaldehydes and two hydroxybenzoic acids were studied by exposing their $5 \mu\text{g/mL}$ water solutions to ozone treatment for increasing time periods. As in previous experiments, 2 mL aliquots of the ozonated solutions were sampled, derivatized and subsequently analyzed by GC-ECNI-MS to determine the concentration of unreacted substrates.

After 40 min treatment, only 42% of the initial 4-hydroxybenzaldehyde was degraded (58% still present), while the remaining concentrations of 2-hydroxybenzaldehyde and 3-hydroxybenzaldehyde were 17% and 30%, respectively. The resulting ozone reactivity toward the three hydroxybenzaldehydes appears to follow the order: 2-hydroxybenzaldehyde > 3-hydroxybenzaldehyde > 4-hydroxybenzaldehyde.

The higher reactivity of 2-hydroxybenzaldehyde is possibly due to the electron-withdrawing properties of the aldehyde group, which deactivates the attack at the ortho- and para- positions: in

2-hydroxybenzaldehyde, the 3- and 5- positions are activated by the OH group and, at the same time, slightly deactivated by the CHO group, in the meta-position. However, the same effects should have been active also for 4-hydroxybenzaldehyde, which was not the case, as 4-hydroxybenzaldehyde turned out to be the least reactive isomer.

The degradation curves for 2- and 4-hydroxybenzoic acids are very similar to one another, due to comparable configuration effects for the two isomers. Both have 3- and 5- positions activated by the hydroxylic group in ortho- and para- to them. Degradation intermediates were identified from both hydroxybenzoic acids, namely 2,3-dihydroxybenzoic and 3,5-dihydroxybenzoic acids from the 2-isomer, and 3,4-dihydroxybenzoic acid from the 4-isomer (Vincenti et al., 2010). These are expected oxidation products, as the OH attack may occur only on the *o*- and *p*- positions with respect to the hydroxylic group.

The 2-hydroxybenzoic acid degradation curve is reported in Fig. 3, showing also the onset and disappearance of the intermediates during the ozonation process. The maximum intermediates' concentration was observed in the first 5 min of ozone treatment. After 20 min, no more intermediates were observed in the reacting solution. A similar trend was observed also for 3,4-dihydroxybenzoic acid, arising from the oxidation of 4-hydroxybenzoic acid.

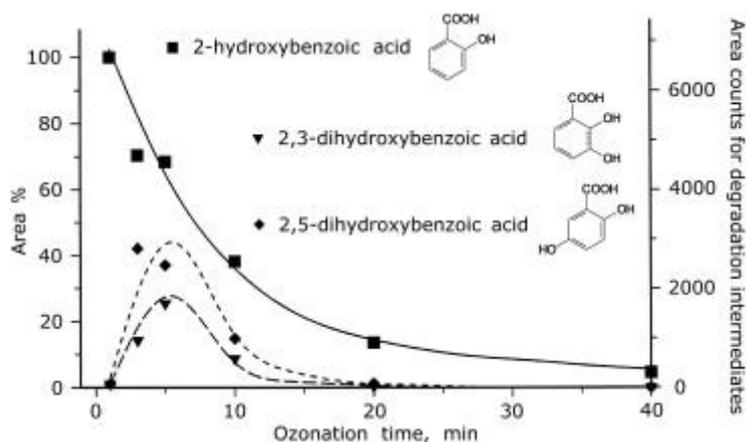


Fig. 3. Degradation kinetics of 2-hydroxybenzoic acid (5.4×10^{-7} mol; ozone 6×10^{-7} mol/min) and evolution of its two intermediates during ozonation treatment. The right y-axis is expanded 250 times.

The slope of the initial segment of degradation curves (when the substrate is present in excess with respect to ozone) provides a rough estimation of the relative reactivities toward ozone for the various substrates studied, including three cresols, three hydroxybenzaldehydes and two hydroxybenzoic acids. The slope values, calculated from the first four points of the curves by the least square method, are reported below:

p-cresol (8.6) > m-cresol (6.3) > 2-hydroxybenzoic acid (6.1) > 4-hydroxybenzoic acid (5.9) > o-cresol (4.1) > 2-hydroxybenzaldehyde (2.0) > 3-hydroxybenzaldehyde (1.6) > 4-hydroxybenzaldehyde (1.3).

It is worth noting that hydroxybenzoic acids and cresols have similar degradation rates despite the electron-withdrawing properties of the carboxylic group. This can be possibly explained by supposing that the reactive species are the dissociated forms (benzoate anions) of hydroxybenzoic acids (pK_a s of 4.1–4.5). On the other hand, the degradation kinetics for hydroxybenzaldehydes are considerably slower than for the corresponding cresols. This difference was expected, considering the electron-withdrawing character of the aldehyde group and the electron-donating properties of the methyl group. This leads to the conclusion that hydroxybenzaldehydes are likely not generated as ozonation products from cresols. In fact, had hydroxybenzaldehydes been produced during ozonation treatment, they would accumulate in solution and be easily determined in the analysis (Vincenti et al., 2010).

3.3. Cresol ozonation products

The oxidation of the cresols by reaction with ozone follows a multistep degradation mechanism, involving the formation of several reaction intermediates until the substrate is potentially mineralized. The identification of reaction intermediates is important in order to understand the main reaction mechanisms and to uncover their possible competition and simultaneous occurrence. The detection of reaction intermediates is difficult because they are frequently more reactive than the initial substrate, yielding no accumulation in the reaction mixture. Thus, extremely sensitive analytical methods are often necessary to determine trace concentrations of these products, which are generally more polar and hydrophilic than the substrate. The analytical method previously developed to detect highly hydrophilic DBPs from ozonation plants (Vincenti et al., 2010), was exploited in the present study to detect intermediate products originating from the reaction of the three cresol isomers with ozone. The results are reported in Table 1. The identification of all the compounds listed in Table 1 was unequivocally ascertained by comparison with pure standards, with the exception of the ones marked with an asterisk (methylmuconic acid, hydroxyitaconic acid), whose structures were proposed on the basis of mass spectral interpretation, as the pure standards were not commercially available. In particular, the mass spectrum of the methylmuconic acid derivative shared the general features of the one obtained for muconic acid, with a 14 Da mass shift for the main ions. Further details on the characteristic mass spectral signals for identified products are reported elsewhere (Vincenti et al., 2010). The identified intermediates were present in at least two solutions produced at different intervals of ozone treatment.

Table 1. Identified degradation intermediates of cresols during ozone treatment. The substances marked with an asterisk were not recognized by comparison with a pure standard, so their identification should be regarded as tentative. Structures of these compounds are shown in Figure S1 in Supplemental material.

o-cresol	m-cresol	p-cresol
Maleic acid	Maleic acid	Maleic acid
Citraconic acid	Citraconic acid	Citraconic acid
Tartronic acid	Tartronic acid	Tartronic acid
Itaconic acid	Itaconic acid	
Malic acid	Malic acid	
	Malonic acid	Malonic acid
	Fumaric acid	Fumaric acid
	4-methylcatechol	4-methylcatechol
2-methylhydroquinone	3-methylcatechol	4-hydroxybenzoic acid
	Methylmuconic acid*	Methylmuconic acid*
	Hydroxyitaconic acid*	Hydroxyitaconic acid*

As an example of an ozonation intermediate identified in the reaction solution of o-cresol, Fig. 4a reports the ECNI mass spectrum of the malic acid derivative. It is produced by reaction of ClOFPCF with the hydroxylic and carboxylic groups of malic acid, to yield the corresponding carbonate and esters, respectively. The product carries three chloro-octafluoropentyl groups imparting high electron affinity to the derivative and resulting in its highly sensitive detection. As is typically observed in ECNI mass spectra, the molecular ion (m/z 922) is undetectable. In its place, an abundant fragment ion at m/z 612 is observed, with an isotopic pattern typical of the presence of two chlorine atoms, which originates by the loss of the carbonate group from the molecular ion. A less intense fragment ion at m/z 576 was also observed, resulting from the loss of HCl from m/z 612. The positive chemical ionization spectrum of the malic acid derivative, depicted in Fig. 4b, contained the molecular ion and many more structurally distinctive ions than the ECNI spectrum, but these ions were barely detectable in the analysis of real reaction mixtures, due to the poorer sensitivity exhibited by the positive ion mode.

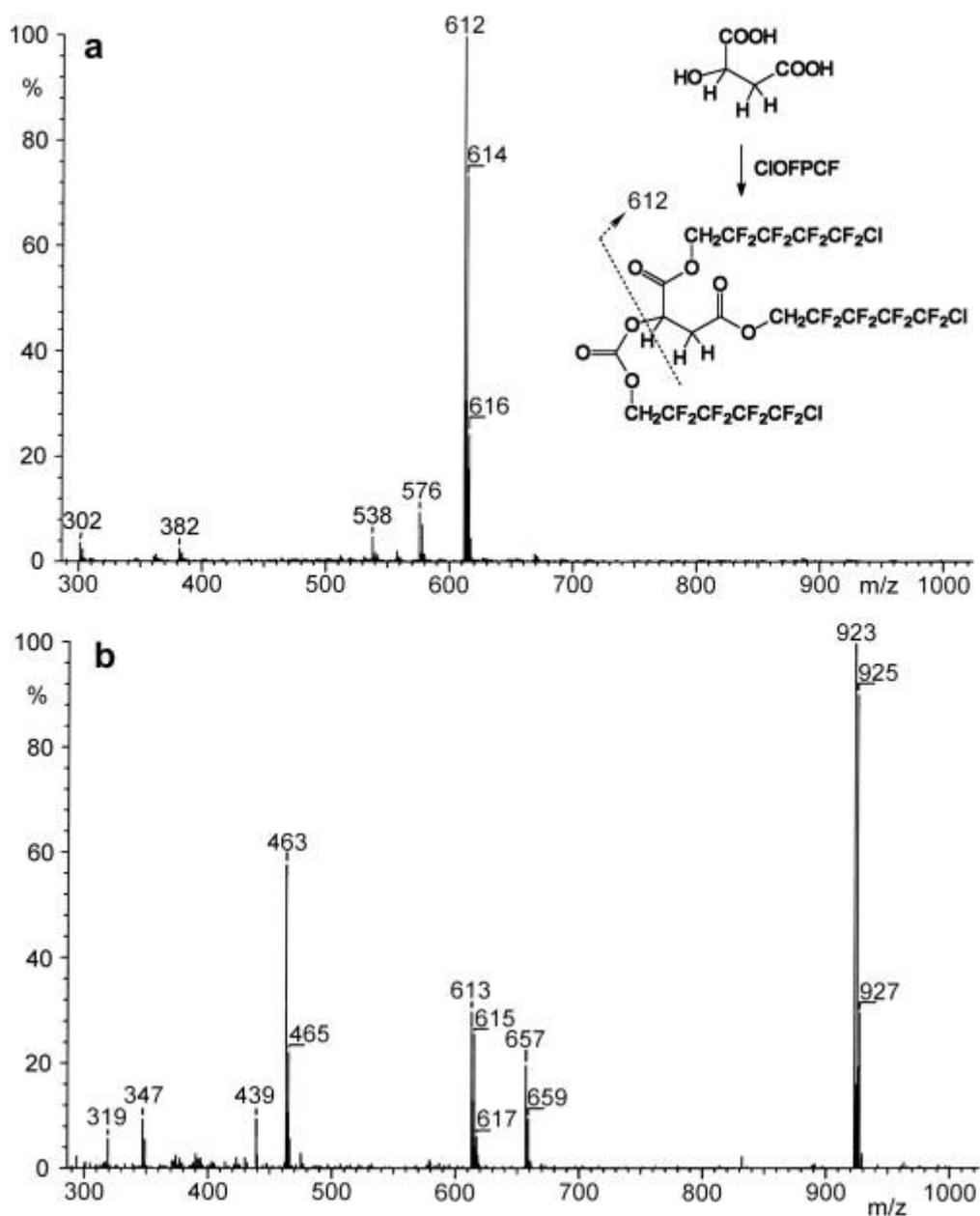
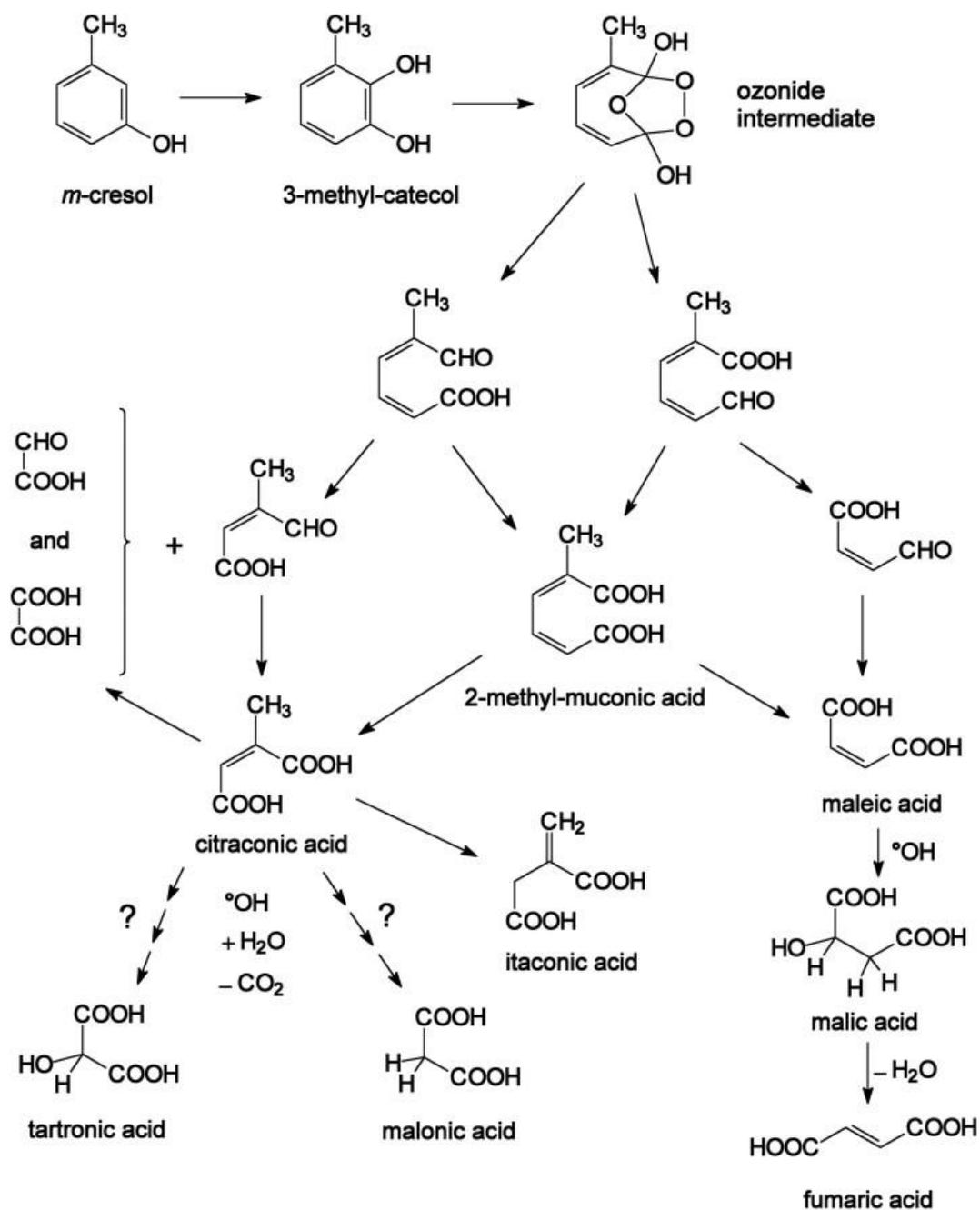


Fig. 4. (a) ECNI mass spectrum of malic acid CIOFPCF derivative; (b) positive chemical ionization mass spectrum of malic acid CIOFPCF derivative.

From the range of identified intermediates (Table 1), it is clear that ozone attack occurs on the aromatic ring and not the methyl group. In fact, almost all the confirmed ozonation products arise from aromatic ring cleavage, while methylcatechols may represent the first step of the oxidation process before ring cleavage. In fact, one or more methylcatechol isomers were constantly present in the reaction mixtures from all cresol isomers. The aromatic ring cleavage generates species containing carboxylic acid and aldehyde groups on opposite sites of the cleaved bond, through formation of the ozonide intermediate (Scheme 1). Subsequent oxidation of the aldehyde group will generate a dicarboxylic acid, such as methylmuconic acid, as was experimentally observed.



Scheme 1. Scheme of the hypothetical oxidative degradation reactions for m-cresol.

After the aromatic ring cleavage, subsequent degradation may occur by different reactions. For example, from the seven-carbon structure of methylmuconic acid (Scheme 1), further attack of ozone on a double bond should generate both five-carbon (citraconic and itaconic acids) and four-carbon compounds depending on the specific double bond attacked. It is worth noting that the identification of seven- and five-carbon cresol oxidation intermediates has been previously reported only by Legube et al. (1981), who determined citraconic acid among the oxidation intermediates of p-cresol. On the other side of the reacting bond, smaller molecules, such as oxalic and glyoxalic acid, are likely to be released (Hsu et al., 2005; Oh et al., 2006; Ramseier and von Gunten, 2009).

A suggested degradation pathway for m-cresol is represented in Scheme 1, where maleic and citraconic acids can be formed from 2-methylmuconic acid. From maleic acid, an $\cdot\text{OH}$ radical attack may sequentially generate malic acid and fumaric acid, after water elimination. Likewise, itaconic acid may be produced by isomerization of citraconic acid, just as fumaric acid is generated from maleic acid (Pimentel et al., 2008). The generation of tartronic and malonic acids cannot be justified by simple reaction mechanisms, such that a combination of different steps, possibly including hydrolysis and CO_2 elimination may be involved. All these substances are likely to represent common disinfection by-products of natural water treated with ozone. For example, two of these intermediates, malic acid and malonic acid, have been reported previously from the ozonation of fulvic acid, humic acid, or natural waters (Anderson et al., 1985; Coleman et al., 1992; Richardson et al., 1999b).

The present experimental data support the three-stage mechanism hypothesized by Hsu et al. (2005) from TOC data for the ozone degradation of 4-cresol and 2-chlorophenol. Hsu proposed that ring-opening of the phenolic unit represented the first step of oxidation, followed by the generation of several intermediate products of increasing oxidation state and leading to relatively stable products, such as oxalic acid, which required long reaction times to be fully mineralized. Similarly, maleic and fumaric acids and, in sequence, succinic and glyoxylic, and lastly oxalic and formic acids were obtained by applying the electrochemical Fenton process to phenols and cresols (Oturán et al., 2008; Flox et al., 2007).

Direct oxidation of the methyl group is likely to occur to a minor extent or not to occur at all, as only trace amounts of hydroxybenzoic acids were detected in the starting unreacted solutions, possibly present as impurities in the substrates. The only exception was observed in the ozonation of p-cresol, where the abundance of 4-hydroxybenzoic acid significantly increased after reaction with ozone.

4. Conclusions

Within the continuous effort to identify unprecedented potentially harmful water DBPs, the reaction of the three cresol isomers with ozone, under disinfection plant simulating conditions, revealed the formation of a variety of highly hydrophilic oxidation intermediates and products (malic, citraconic, maleic, malonic, fumaric and tartronic acids), some of which have never been previously reported (methylmuconic acid, itaconic acid). Although most of these products can be generated from the ozonation of several aromatic substrates, including substituted phenols, and also from the oxidation of cresols by photoelectrochemical Fenton treatments (Pimentel, 2010; Flox et al., 2007), the characterization of cresols' degradation products was generally limited to those preceding ring cleavage (Wang et al., 1998; Olariu et al., 2002; Coeur-Tourneur et al., 2006). Ring cleavage by-products generally originate in the final steps of an extensive oxidation process and are possibly

too polar and hydrophilic to be efficiently extracted from the water matrix and/or detected with reasonable sensitivity. Therefore, the formation of degradation products, such as small polycarboxylic and hydroxycarboxylic acids, has frequently been proposed in the past, but only occasionally demonstrated (Legube et al., 1981). Application of our original analytical approach based on the direct derivatization in water of these compounds, by means of highly hydrophobic chloroformates, provided an innovative tool to investigate the multistep process of complex oxidation mechanisms such as the ozonation of cresols.

We also demonstrated that the methyl group of cresols is a disfavored site of initial ozone attack, unlike what is observed in TiO₂ photocatalysis (Wang et al., 1998). In contrast, the wide range of identified intermediates supports a degradation mechanism involving the initial oxidation of the ring, followed by ring-opening and consecutive double bond cleavages, possibly by molecular ozone attack.

The substances identified in this study are likely to represent common disinfection by-products of natural water treated with ozone. These products do not raise concern about their potential toxicity, as many of them are naturally present in a variety of foods and are not expected to be toxic, but the analytical approach used in the present study is likely to reveal more harmful compounds in the future, for example highly polar halogenated DBPs.

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